INSIGHT IN NUCLEATION MECHANISMS OF SEMICONDUCTING 2D METAL SULFIDES – APPLICATION TO AREA SELECTIVE DEPOSITION

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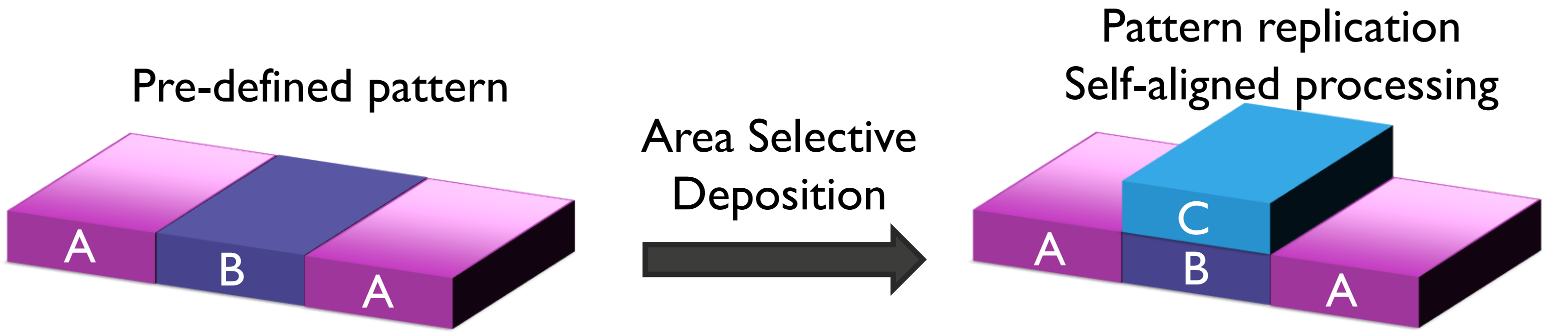
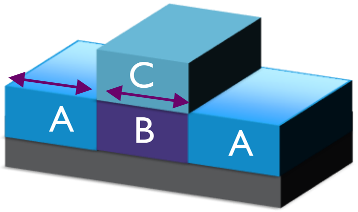
BOTTOM UP APPROACHES FOR PATTERNING

- Scaling brings significant challenges in patterning: Resolution, accurate pattern placement
- Bottom-up approaches combined with conventional top-down patterning
  - Self-aligned multiple patterning
  - Directed self-assembly
  - **Area Selective Deposition (ASD)**

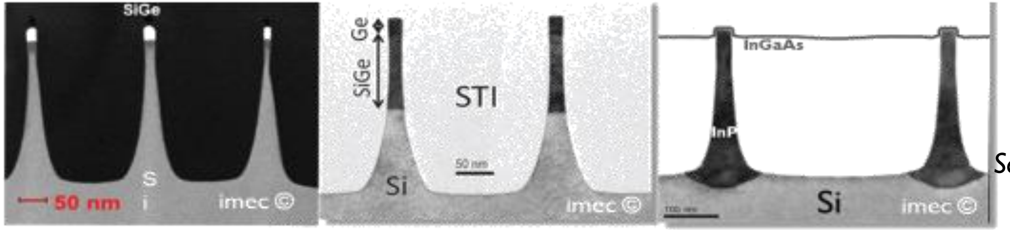


ASD – STATE OF THE ART



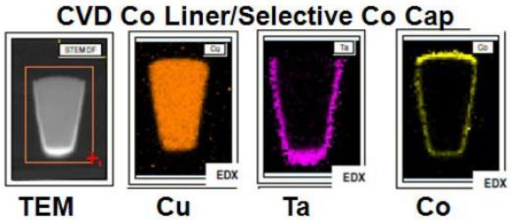
e.g. Loo et al, *ECS J. Solid State Science and Technology*, 6, P14 (2017)

Semiconductor on semiconductor



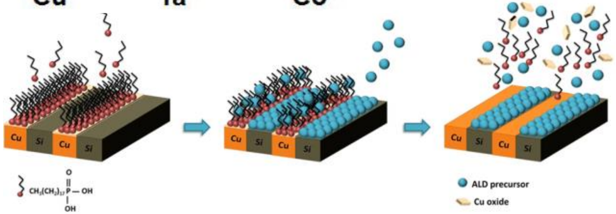
Metal on Metal (MoM): Few demonstrations

- Capping layers (Co, Mn …) on Cu (electro-migration)
- Selective bottom up fill with ELD (Co)



Simon et al, *IEEE IRPS*, 2013

Dielectric on Dielectric (DoD)
Few studies on (sub)micron scale, limited materials, limited characterization of selectivity



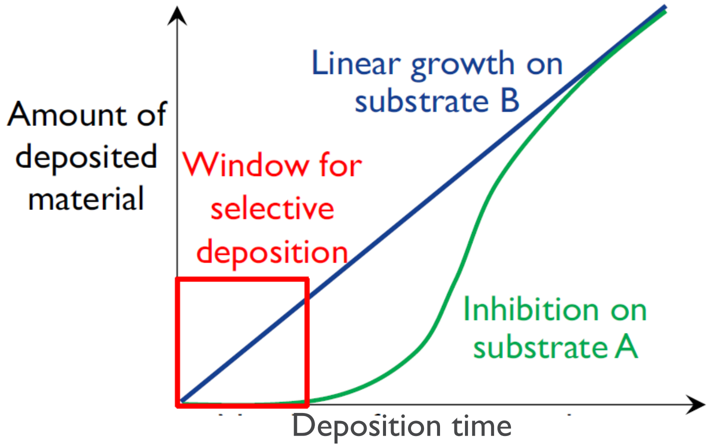
Minaye Hashemi et al, *ACS Nano*, 9, 8710 (2015)

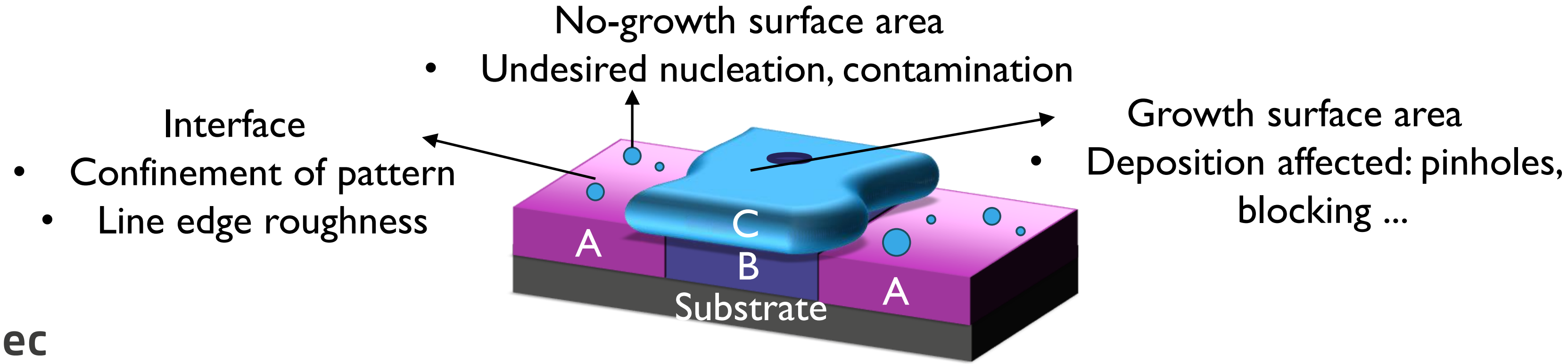
Metal on Dielectric selective to Metal (MoD)
Dielectric on Metal selective to Dielectric (DoM)

?

AREA SELECTIVE DEPOSITION – GOALS

1. Expand material systems accessible by ASD
   - Semiconductor, metal, metal oxide, 2D material
   - Surface dependence of ALD, CVD, ELD
2. Achieve sufficient selectivity for applications in patterning, at sub-30nm dimensions
   - Surface composition changes after patterning
   - Impact of processes growth/no-growth surface area
   - Characterization of selectivity

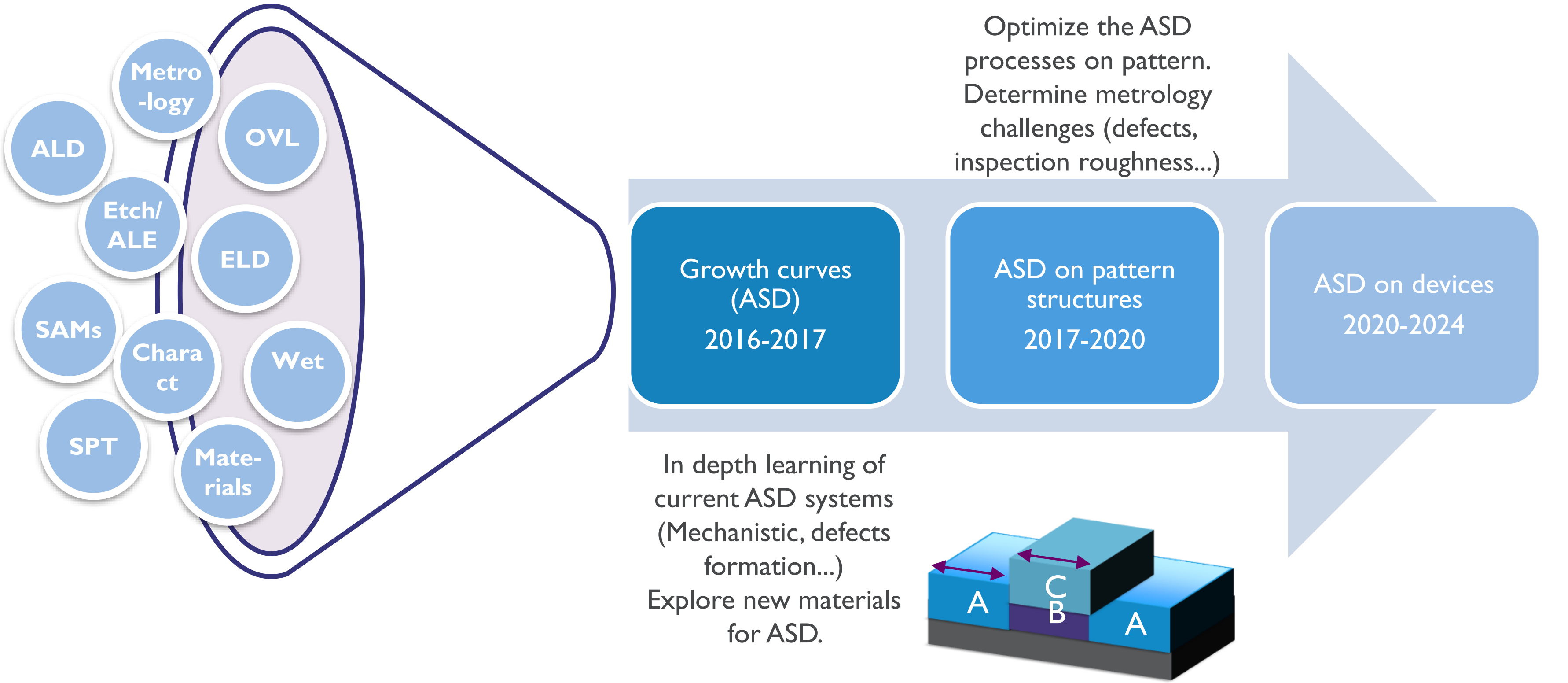




ASD FOR FUTURE TECHNOLOGIES

KNOWLEDGE NEEDS TO BE BUILT UP AT RELEVANT DIMENSIONS

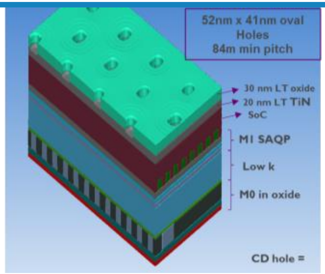
Efrain Altamirano Sanchez

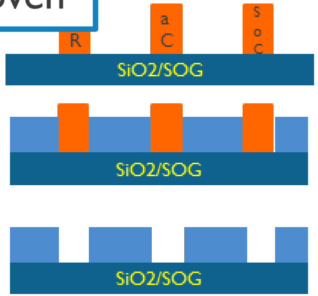


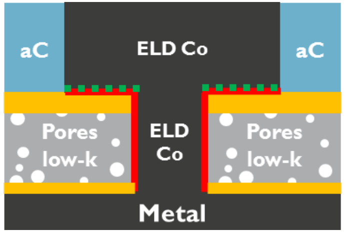
AREA SELECTIVE DEPOSITION (ASD) FOR FUTURE TECHNOLOGIES

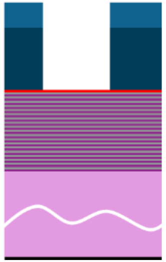
See also Ivan Zyulkov, Job Soethoudt, Benjamin Groven

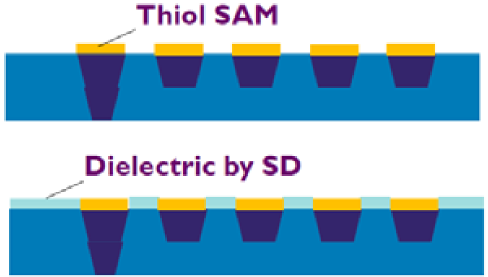
- Tone reversal patterning solutions
  - DoM/MoM/MoD for Block Mask BEOL, DoD
- Bottom up fill for future interconnect
  - Partial via fill, BEOL: MoM: Ru on Co/Ru, not on low-k
  - Trench fill, BEOL MoD: Ru on SiCN not on aC. Ru catalyst for Co ELD
- Bottom up fill for EUV mask absorber: Co, Ni, CoNi fill by ELD on Co/Ru not on SiO_2
- Self aligned via (DoD, BEOL)
- Processes for new 3D device architectures (e.g. 3D VFET or VSRAM)
- Deposition of 2D semiconductors









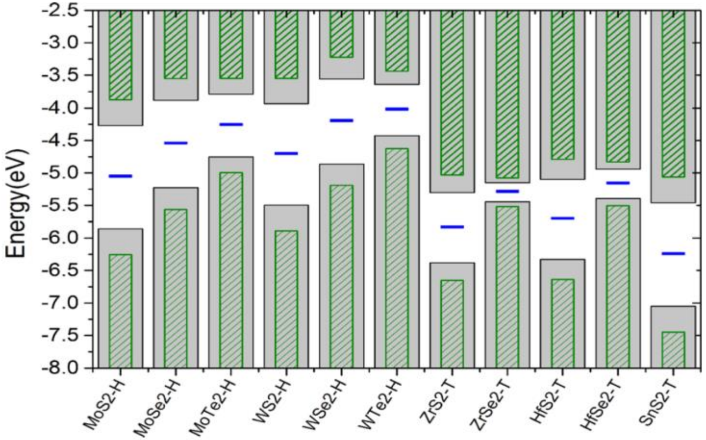


2D MATERIALS BEYOND GRAPHENE

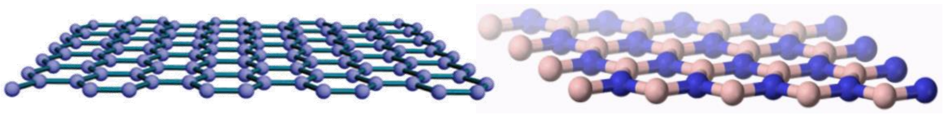
Diversity of 2D structures, compositions, properties available for exploration

Atomically thin 2D semiconductors

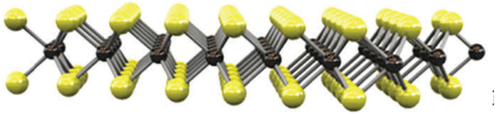
- Fully passivated semiconductor interface
- Reduced short channel effects
- Choice of bandgaps and band alignment → hetero-stacks for TFET



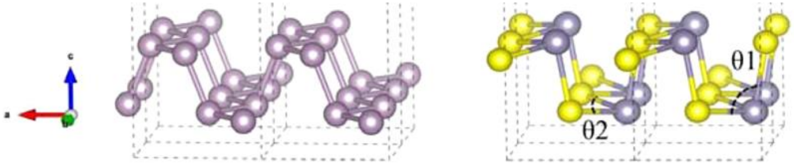
Graphene & analogues e.g. h-BN



Transition Metal Dichalcogenides (MX_2)
e.g. MoS_2, WS_2, WSe_2



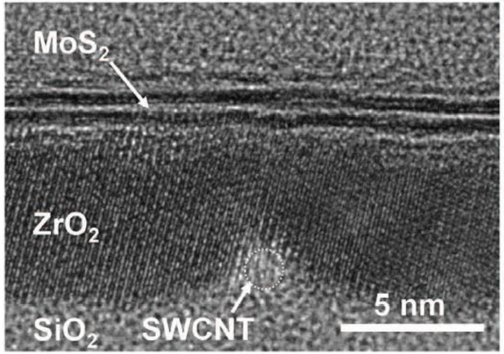
Black Phosphorous & analogues e.g. SnS, SnSe



P. Miro et al, An atlas of two-dimensional materials, *Chem. Soc. Rev.*, 43, 6537 (2014)
C. Gong et al., *Appl. Phys. Lett.* 107, 139904 (2015)

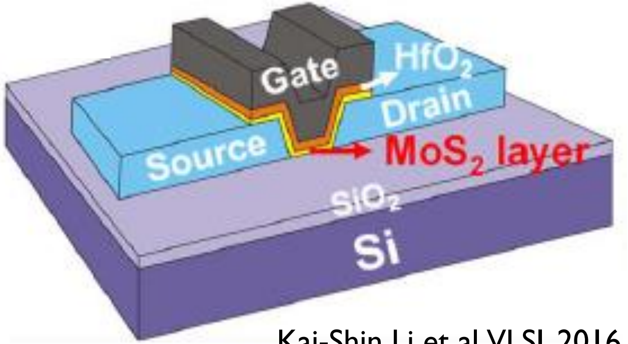
EXPLORATION OF 2D MATERIALS IN NANO-ELECTRONIC DEVICES

MOSFET with 1nm gate length

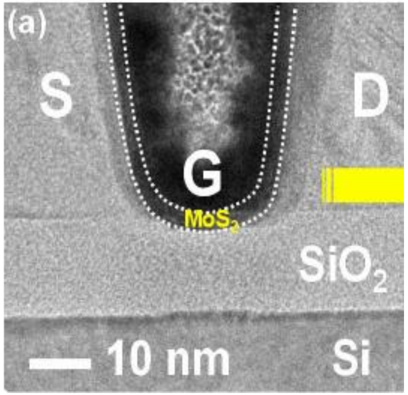


Desai et al., *Science*, 354, 2016

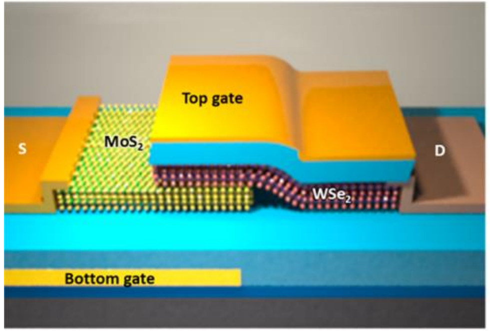
MoS_2 U-shape MOSFET



Kai-Shin Li et al, VLSI, 2016

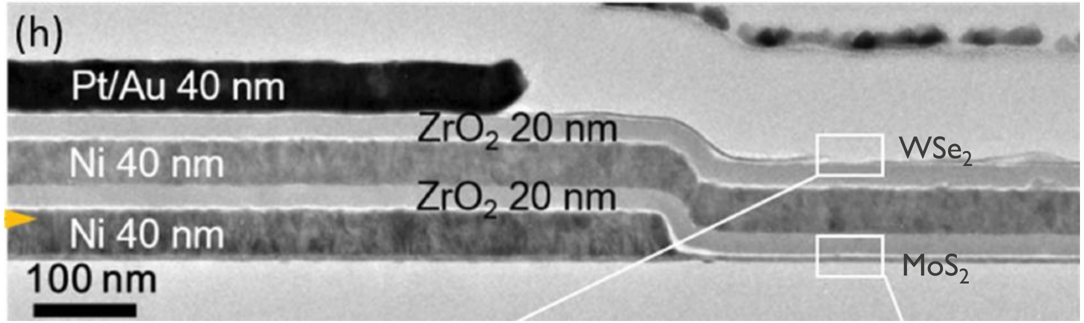


TFET



T. Roy et al., *ACS Nano*, 9, 2071, 2015

Monolithic 3D integration (BEOL)

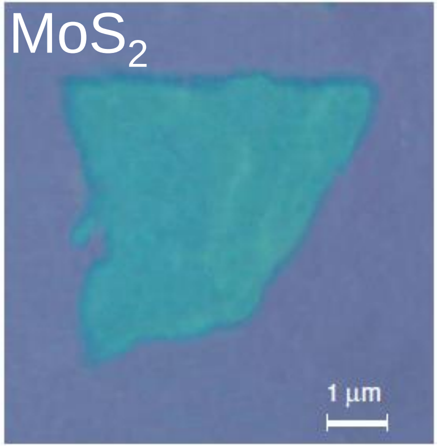


A. B. Sachid et al, Adv. Mater. **2016**, *28*, 2547–2554

FABRICATION PROCESSES FOR 2D MATERIALS

Exfoliation from natural crystals and transfer

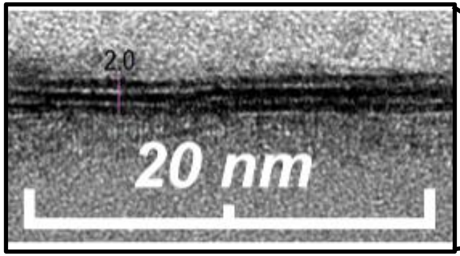
- Exploration of 2D materials, proof of concept
- Limited area - micrometers



MX_2 deposition techniques Atomically Controlled Deposition

- Industrial applications
- Large area substrates

Benjamin Groven and Markus Heyne, PhD students at imec 2D WS_2 deposition on 300mm wafers



FABRICATION PROCESSES FOR 2D MATERIALS

CHALLENGES

- Semiconducting properties – high quality structure, crystallinity
  - Monocrystalline, exclude impact of grain boundaries
  - Low vacancy, defect, impurity content
- Monolayer growth control on large area substrates
  - From few down to single monolayers
  - Van der Waals hetero-structures
- Conformality
- Temperature budget ~ integration flows

OPTIONS

- MX_2 deposition techniques
  - Sulfurization of metals or oxides
  - Chemical Vapor Deposition (CVD)
  - Atomic Layer Deposition (ALD)
  - Molecular Beam Epitaxy (MBE)
- Different integration schemes
  - Transfer
  - Template
  - Top down → Bottom up

MX_2 BY CHEMICAL VAPOR DEPOSITION (CVD)

Monolayer thin crystals with lateral size up to millimeter on SiO_2 substrates

State of the art optical and electrical properties, comparable to exfoliation

Moderate deposition temperatures (450 – 700°C)

Challenges:

- Polycrystalline in absence of template for epitaxial seeding
- Monolayer growth control, uniformity on large area substrates

Y. Gong et al, Adv. Funct. Mater. **2016**, 26, 2009

Van der Zande et al, *Nature Materials*, 12, 554, 2013

~ mm (→ Max single crystal size)

Monolayers	Band gap (eV)	Max polycrystalline film size	Max single crystal size	Max mobility on SiO_2/Si ($cm^2 V^{-1} s^{-1}$)
Graphene	0	40 inches[80]	5.08 cm[61]	16 000[77]
hBN	~6.0	7 cm × 7 cm[88]	~10 µm[90,91]	—
MoS_2	~1.8	1 cm × 3 cm[92]	~123 µm[93]	7[94]
WS_2	~2.1	1 cm × 1 cm[95]	~180 µm[96]	0.46[97]
$MoSe_2$	~1.5	1.5 cm × 2 cm[98]	~135 µm[99]	50[99]
WSe_2	~1.7	~1 inch[100]	~50 µm[100]	90[100]

H. Wang et al, *Nanoscale*, 2014, 6, 12250

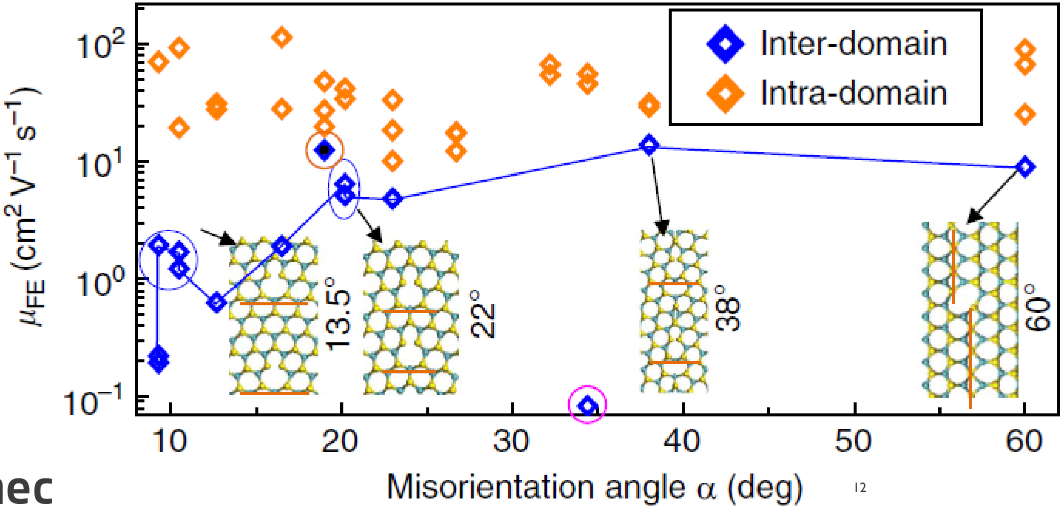
GRAIN BOUNDARIES IN POLY-MX_2 DEGRADE CARRIER MOBILITY

CVD deposited 2D TMDs are polycrystalline in absence of template for epitaxial seeding

Grain boundaries degrade the carrier mobility of MoS_2

- Intra-domain mobility: 44 $cm^2V^{-1}s^{-1}$ (17-115 $cm^2V^{-1}s^{-1}$, as for exfoliated MoS_2)
- Inter-domain mobility: max 16 $cm^2V^{-1}s^{-1}$, 2 orders of magnitude dependence on misorientation angle

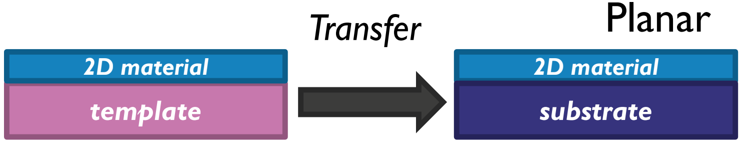
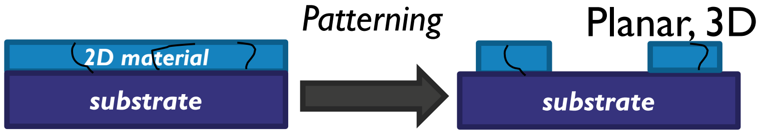
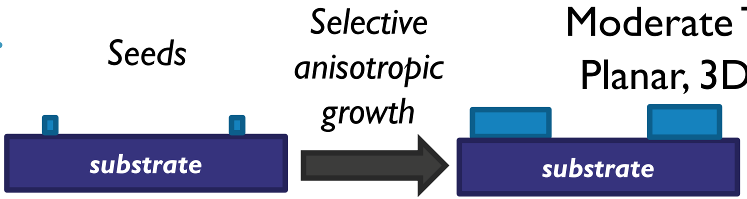
How can we avoid impact of grain boundaries between randomly oriented crystals ?



Atomic defect structures (TEM) of measured devices and first-principles calculations

Ly et al, *Nature Communications*, 7, 10426 (2016)

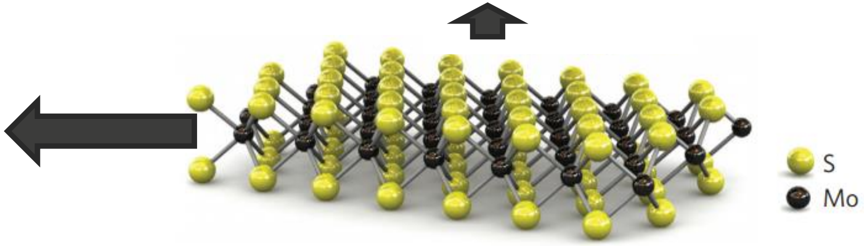
MX_2 GROWTH – INTEGRATION SCHEMES

Integration scheme	Conditions	Structural implications	Technique
1. **Top down – Transfer**  	Template High T Planar	**Monocrystalline films, high structural quality** Impact transfer: contamination, structural damage, alignment of hetero-stacks	Epitaxy by high-T CVD (MBE)
2. **Top down – No transfer**  	No template Moderate T Planar, 3D	**Polycrystalline films** Maximize grain size to minimize impact of randomly located grains and grain boundaries	CVD (ALD)
3. **Bottom up – No transfer**  	No template Moderate T Planar, 3D	**Grain boundaries outside device area by controlled seeding** Crystal size ~ device dimensions, self-aligned processing	CVD (ALD)

OPPORTUNITIES FOR SELECTIVE DEPOSITION OF 2D MATERIALS

- Anisotropy in bonding and reactivity in 2D materials → unique opportunity for selective anisotropic growth
  - Crystal edges are more reactive than the fully passivated basal plane
- Versatile chemistry of halide precursors in CVD, ALD
  - High purity films
  - Area selective deposition

Anisotropy in bonding and reactivity



WF_6 for WS_2 ALD, CVD
$SnCl_4$ for SnS_2 and SnS CVD

Understanding of the growth and nucleation mechanisms of 2D materials
→ Design of bottom-up synthesis approaches for 2D materials

OUTLINE

- Area selective deposition of WS_2 – New concept for selective deposition by conversion of sacrificial patterns
- Understanding of nucleation mechanisms of CVD and ALD processes → Opportunities for selective anisotropic growth

ALD AND CVD OF 2D WS_2

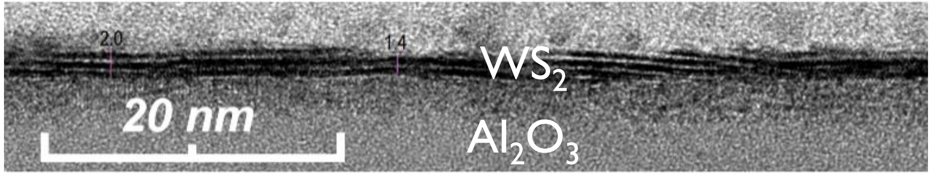
Thin WS_2 layers with 2D structure can be obtained at low deposition temperature, without using a template for epitaxial seeding

Low temperature deposition enabled by reducing agents

$WF_6 + H_2S$

H_2 plasma

PEALD (300-450°C)

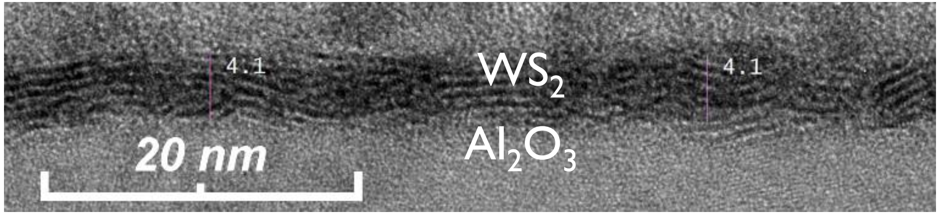


A. Delabie et al., *Chem. Commun.*, 51, 15692 (2015)

B. Groven et al, *Chemistry of Materials*, 10.1021/acs.chemmater.6b05214 (2017)

Sacrificial Si layer

Pulsed CVD (450°C)



A. Delabie et al., *Chem. Commun.*, 51, 15692 (2015)

M. H. Heyne et al, *Nanotechnology*, 28, 04LT01 (2017)

CVD WS_2 GROWTH MECHANISM → SELECTIVE DEPOSITION

WS_2 CVD at 400-450˚C is enabled by Si sacrificial layer (reducing agent)

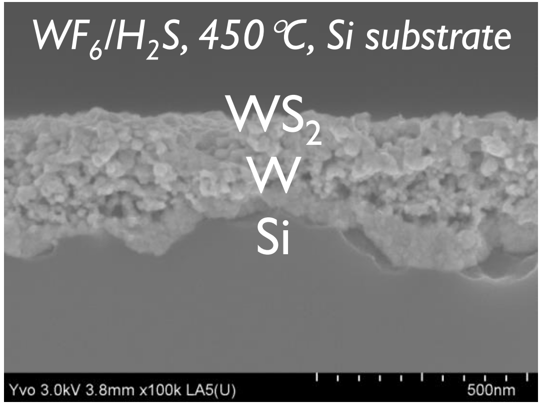
$$2\,WF_{6(g)} + 3\,Si_{(s)} \rightarrow 2W_{(s)} + 3\,SiF_{4(g)}$$

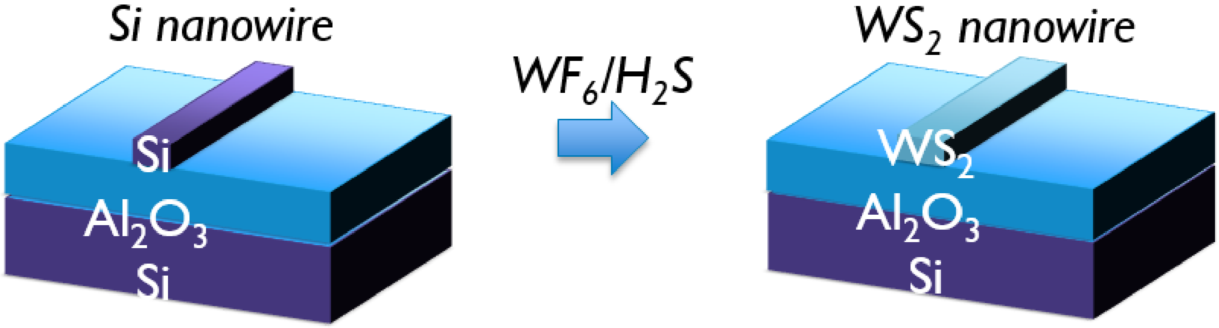
$$W_{(s)} + 2\,H_2S_{(g)} \rightarrow WS_{2(s)} + 2\,H_{2(g)}$$

No WS_2 deposition by sequential WF_6/H_2S reactions on several dielectric layers

→ WS_2 thickness control by thickness of Si layer on dielectric

→ Area selective deposition on dielectric for sacrificial Si pattern with under layer

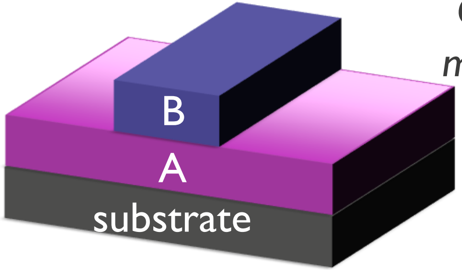




CONCEPTS OF AREA SELECTIVE DEPOSITION

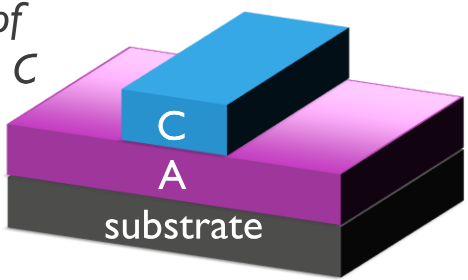
Selective conversion of sacrificial patterns

Patterned sacrificial layer B



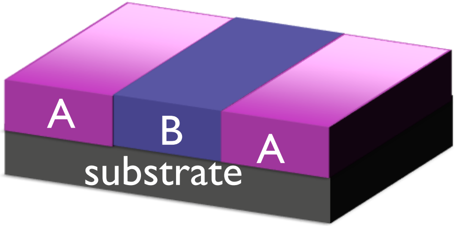
Conversion of material B to C

Selective conversion



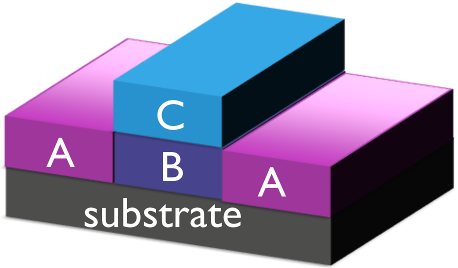
Area selective deposition

Pre-defined pattern A/B



Selective Deposition

Pattern replication
Self-aligned deposition of C on B



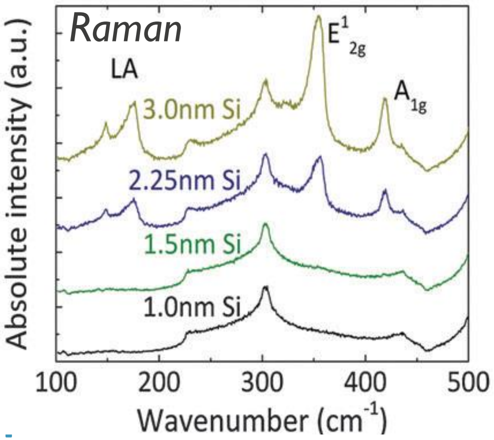
WS_2 PULSED CVD (450°C) WITH SI SACRIFICIAL LAYER (MBD, PVD)

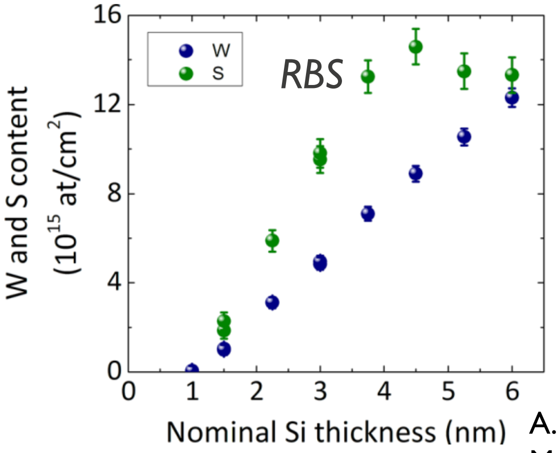
Crystalline 2D WS_2 formed by sequential reactions of WF_6 and H_2S and a sacrificial Si layer (RAMAN, XPS, XRD)

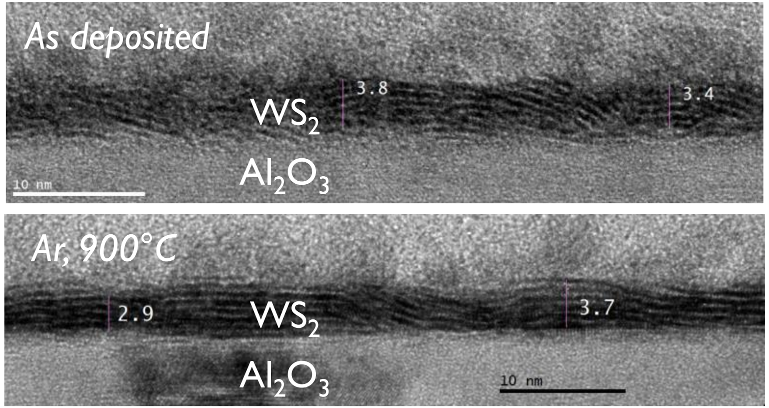
WS_2 thickness control by thickness Si layer (RBS)

2D structure of WS_2, nano-crystalline (grain size ~5nm), random orientation

Rapid thermal annealing (Ar, 900°C) improves horizontal layer alignment

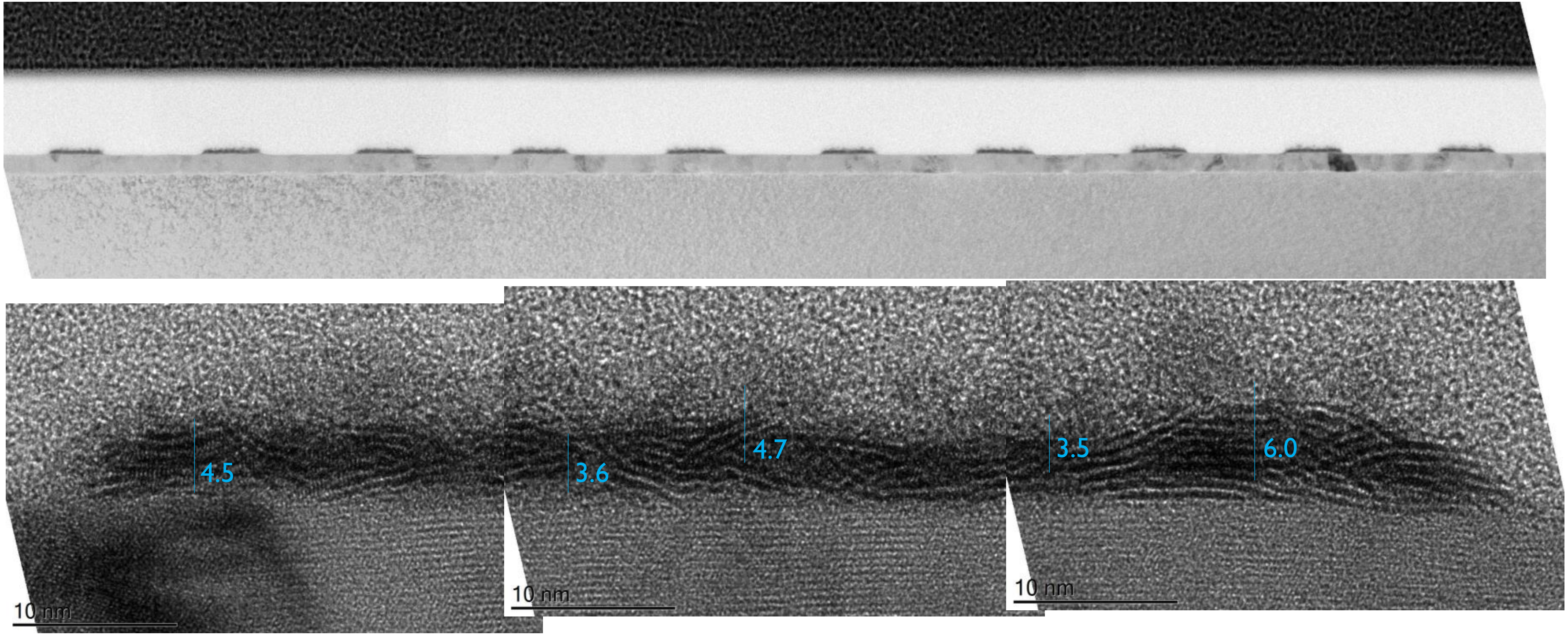






A. Delabie et al., *Chem. Commun.*, 51, 15692 (2015),
M. H. Heyne et al, *Nanotechnology* 28 (2017) 04LT01

PROOF OF CONCEPT: AREA SELECTIVE DEPOSITION OF 2D WS_2
BY SELECTIVE CONVERSION OF SACRIFICIAL SI LINES



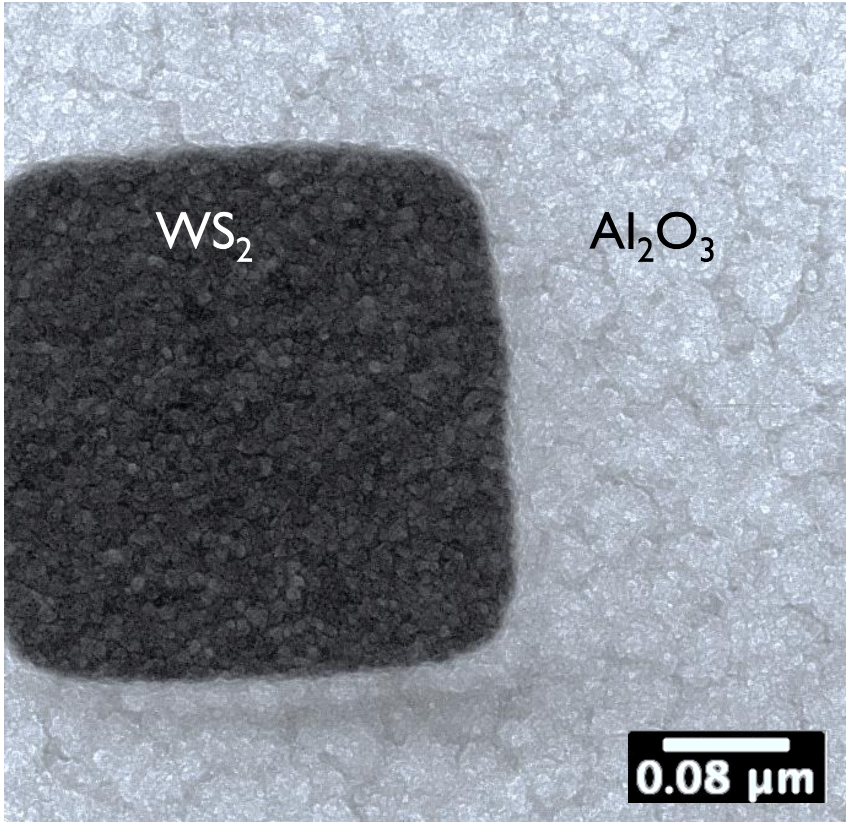
M. H. Heyne et al, *Nanotechnology* 28 (2017) 04LT01

PROOF OF CONCEPT: AREA SELECTIVE DEPOSITION OF 2D WS_2

BY SELECTIVE CONVERSION OF SACRIFICIAL SI STRUCTURES

W. Vandervorst et al, ASD workshop 2016, Imec, Belgium

- Conversion of Si to WS_2 on Al_2O_3 is highly selective, as indicated by Helium Ion Microscopy (HIM, sub-nanometer resolution)
  - No WS_2 grains on the Al_2O_3 field
  - Si patterning is well established – clean Al_2O_3 top surface
- Small grain size of WS_2 in 300nm x 300nm pattern (~10nm) on polycrystalline Al_2O_3
- Decrease of lateral dimensions might enable deposition of monocrystalline WS_2 seeds for controlled seeding



OUTLINE

- Area selective deposition of WS_2 – New concept for selective deposition by conversion of sacrificial patterns
- Understanding of nucleation mechanisms of CVD and ALD processes → Opportunities for selective anisotropic growth

ALD AND CVD OF 2D WS_2

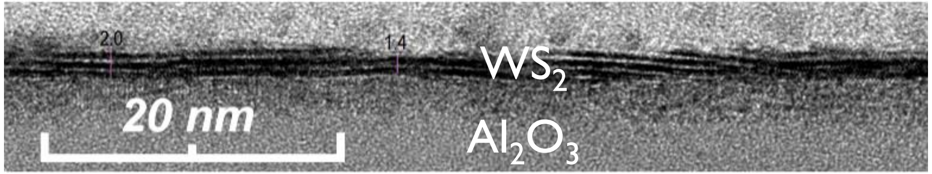
Thin WS_2 layers with 2D structure can be obtained at low deposition temperature, without using a template for epitaxial seeding

Low temperature deposition enabled by reducing agents

$WF_6 + H_2S$

H_2 plasma

PEALD (300-450°C)



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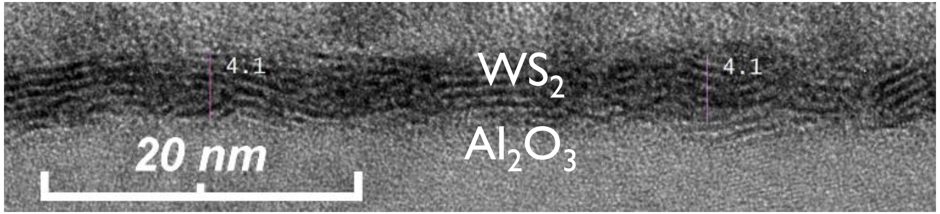

A. Delabie et al., *Chem. Commun.*, 51, 15692 (2015)

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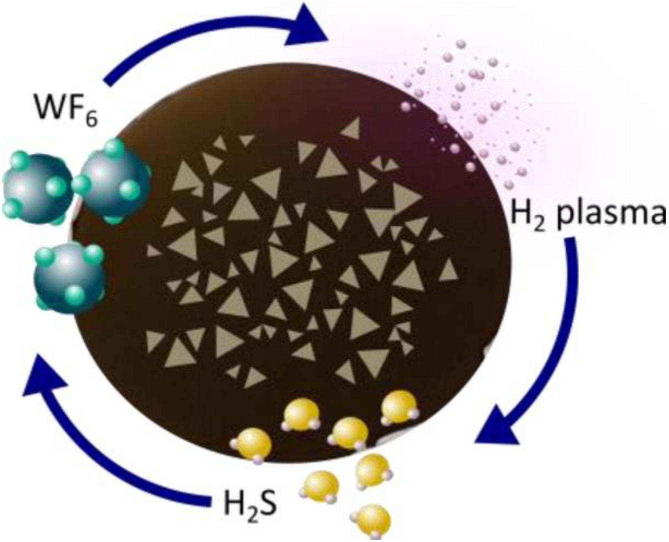
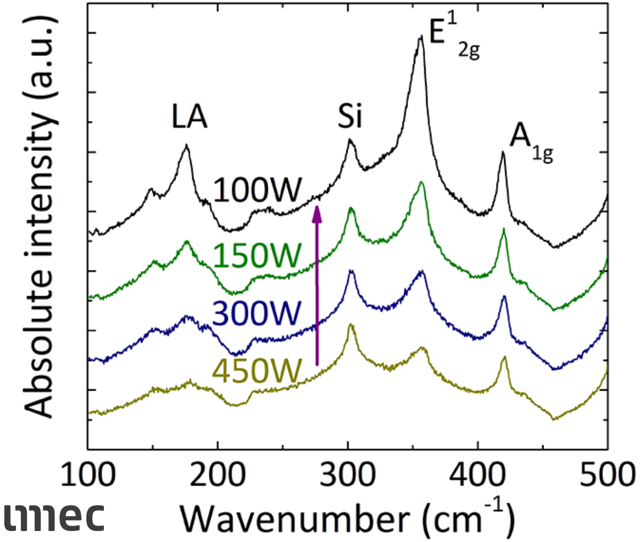
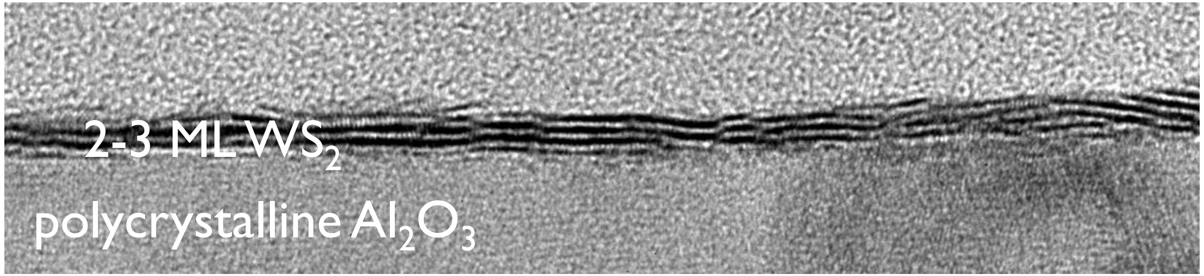
WS_2 PEALD – 2D STRUCTURE

- Strongly textured, polycrystalline WS_2 layers are obtained at low T (300–450°C) without using a template or anneal
- Crystallinity (grain size, in-plane alignment) depends on nucleation mechanisms



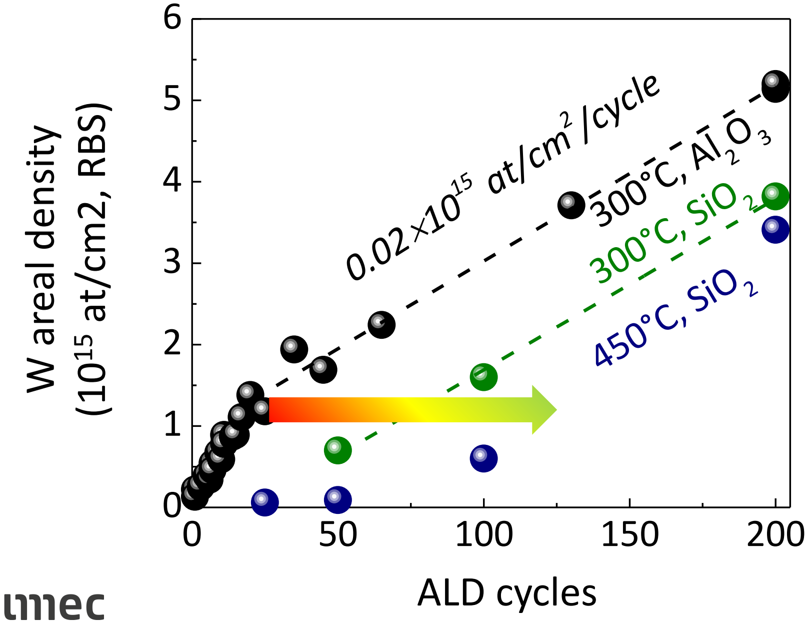




B. Groven et al, *Chemistry of Materials*, 10.1021/acs.chemmater.6b05214 (2017)

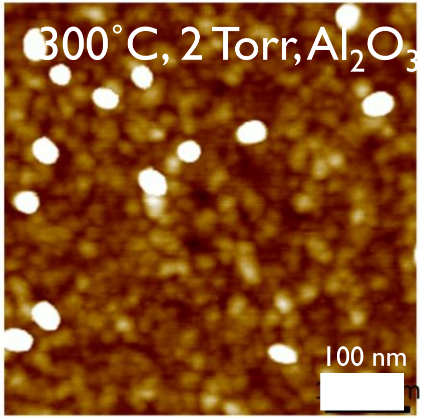
PEALD WS_2: 2D STRUCTURE ⇔ NUCLEATION MECHANISMS

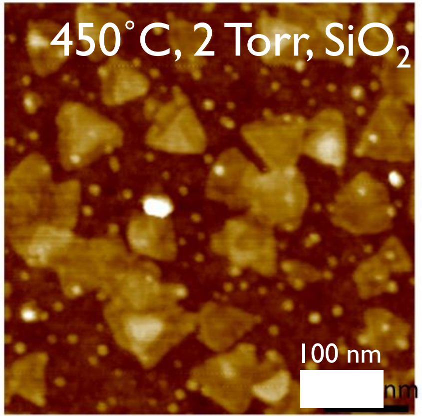
Nucleation and grain size depend on
- Reactivity of substrate (SiO_2, Al_2O_3)
- Deposition temperature



		Nucleation density (/cm²)	Grain size (nm)
300°C	Al_2O_3	10^{14}	5-30
	SiO_2	10^{11}	10-40
450°C	SiO_2	10^{10}	50-100

AFM in early growth stage → grain size, nucleation density

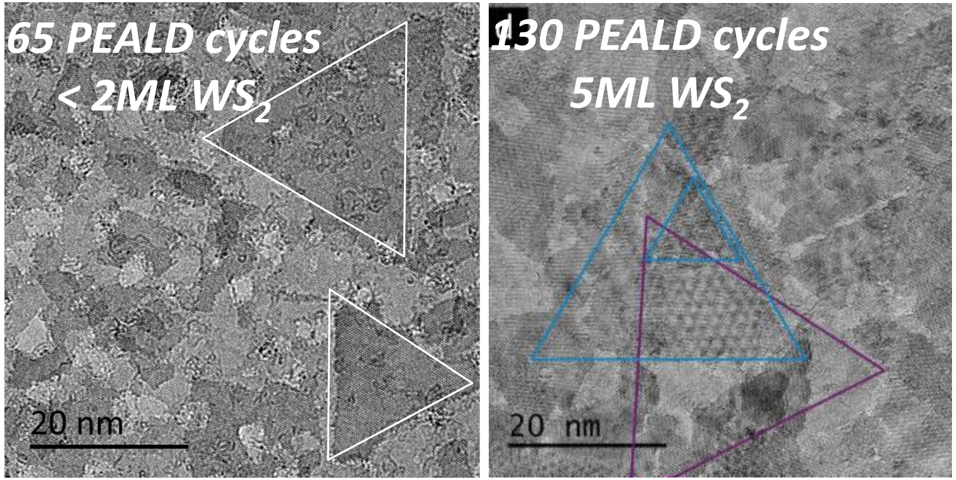


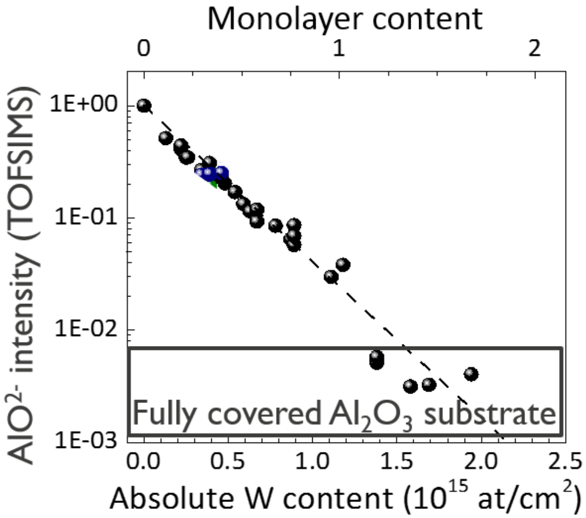


PEALD WS_2 NUCLEATION BEHAVIOR – CRYSTALLINITY

- High nucleation density on Al_2O_3 (E+14/cm^2) → nano-crystalline WS_2 (5-30nm grain size)
- Random in-plane orientation of layers (Moiré patterns): precursor adsorption on grain boundaries and WS_2 basal planes
- Preferential adsorption on Al_2O_3 does ensure rapid layer closure of WS_2 layer (< 2 ML, plane view TEM, TOFSIMS)

Plane view TEM



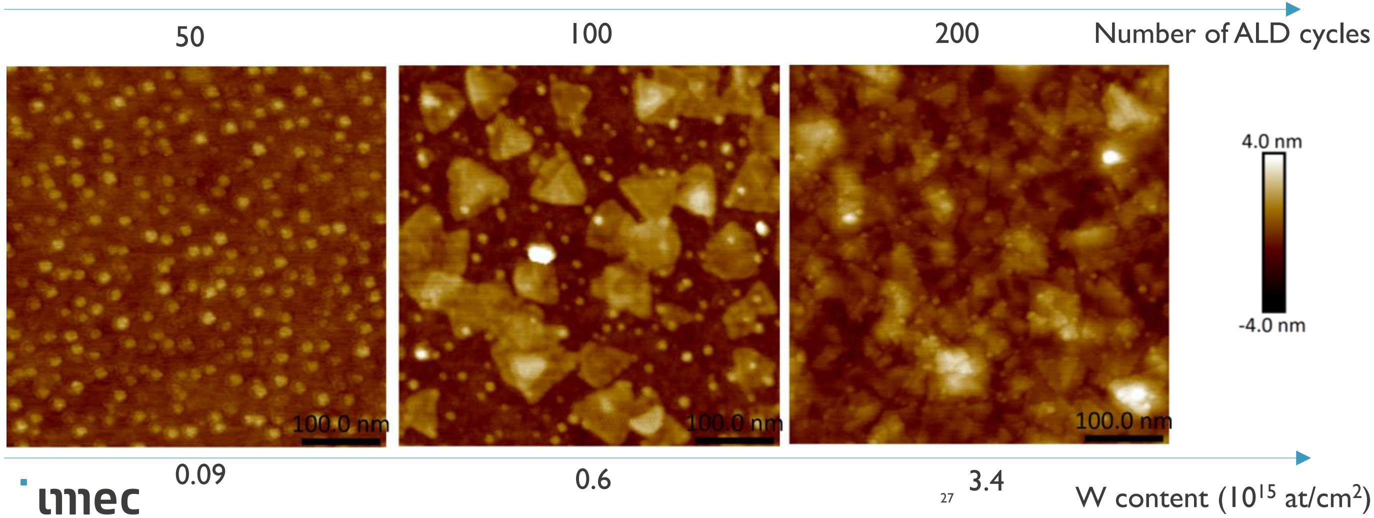


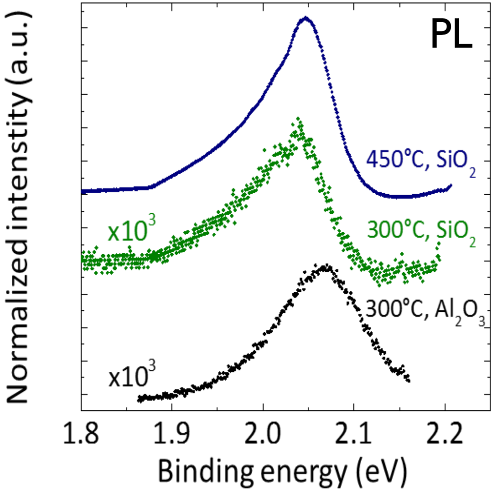
PEALD WS_2: NUCLEATION BEHAVIOR ⇔ 2D STRUCTURE

WS_2 domain size increases to ~100nm by decreasing the nucleation density: less reactive substrate (SiO_2) and higher T (450°C)

2D crystals with controlled in-plane alignment (on first WS_2 layer of crystal) → >10^4 orders of magnitude increased PL intensity

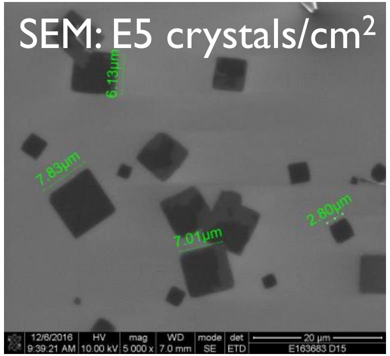
Both vertical and horizontal growth contributions

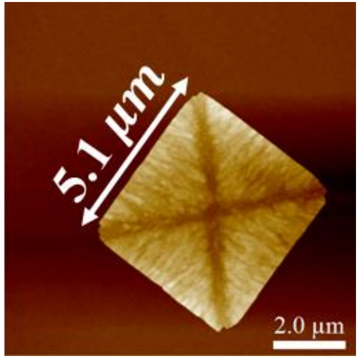


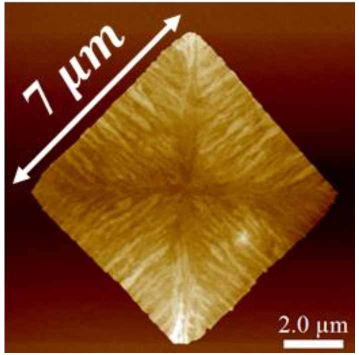


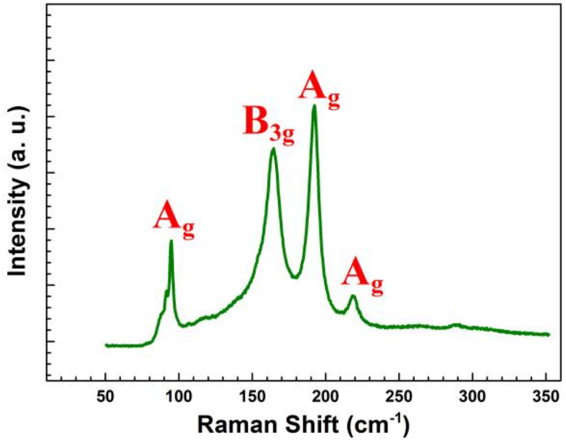
CVD OF 2D SnS CRYSTALS

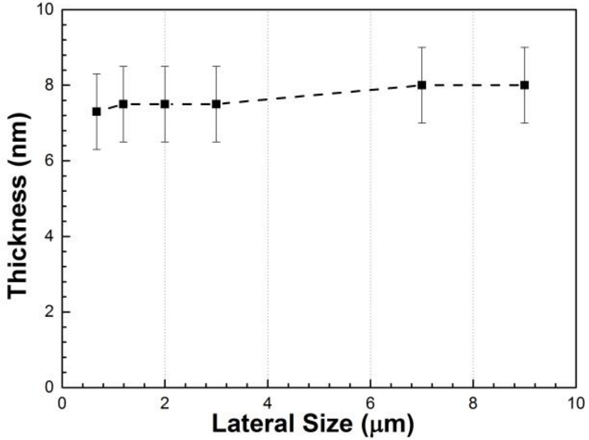
- Low nucleation density (E5 crystals/cm^2 << E10 crystals/cm^2 for PEALD)
  - Lateral dimensions of SnS crystals: micrometer scale
- Fixed height of SnS crystals (6-8nm) for different lateral sizes (AFM)
- Nucleation mechanisms for SnS (and SnS_2) CVD on SiO_2: island formation and selective horizontal growth









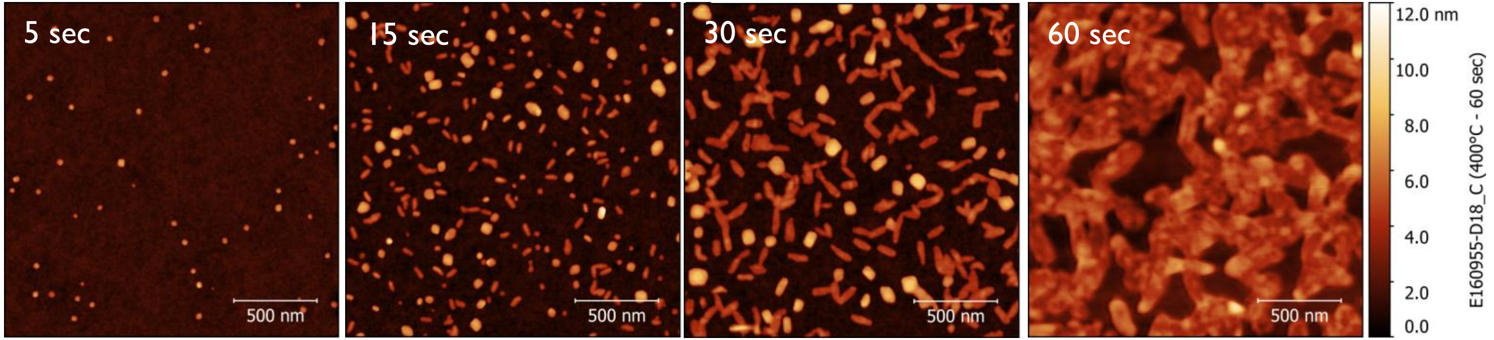


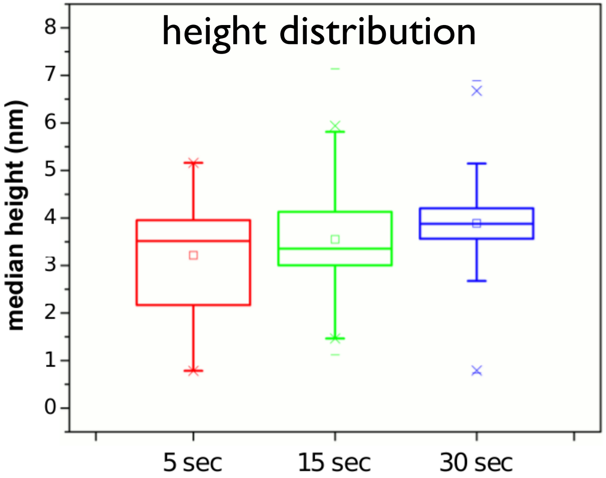
NUCLEATION MECHANISM OF SnS_2 CVD

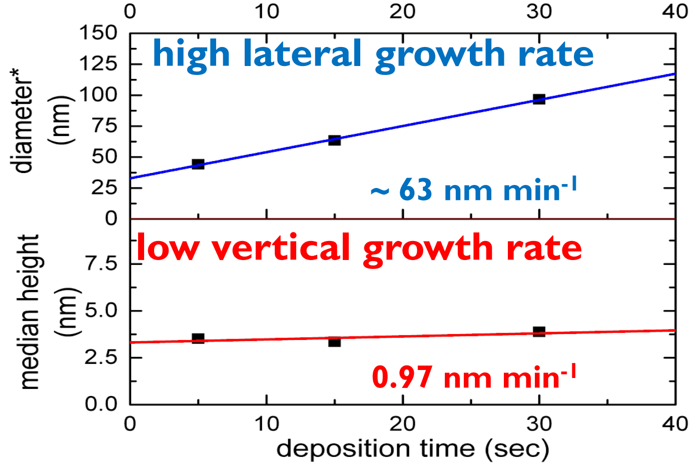
SnS_2 surface coverage and grain size increases with constant height of SnS_2 crystals (4 nm)

→ **Selective horizontal growth**, higher reactivity of crystal edges versus basal planes

AFM







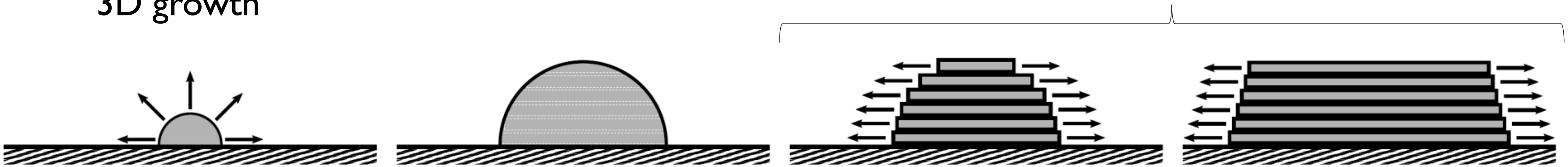
NUCLEATION MECHANISM OF SnS_2 AND SnS CVD

- Initial nucleation regime on SiO_2 substrate before layer closure: island growth, formation of 2D crystals and selective lateral growth
- Height of 2D crystals is determined by initial nucleation mechanisms (SnS_x islands, composition and phase)

Adsorption of $SnCl_4/H_2S$ on SiO_2 surface
Formation of initial SnS_x nuclei
3D growth

Critical dimension: 2D structure, horizontal basal planes

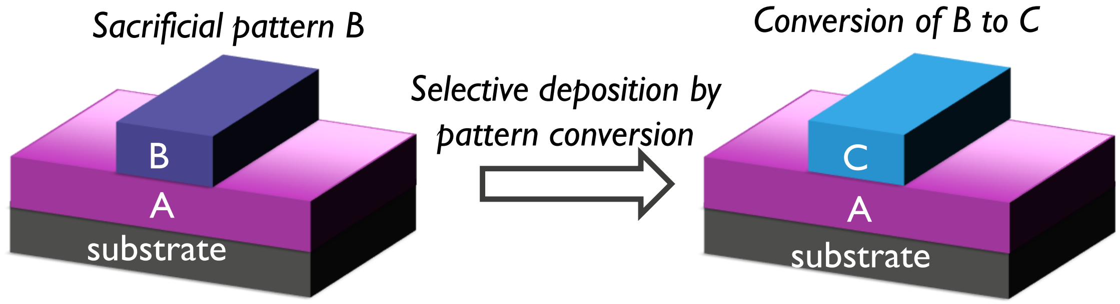
Directional growth, 2D growth, **selective horizontal growth** due to higher reactivity of crystal edges and SiO_2 surface versus basal planes
Until layer closure



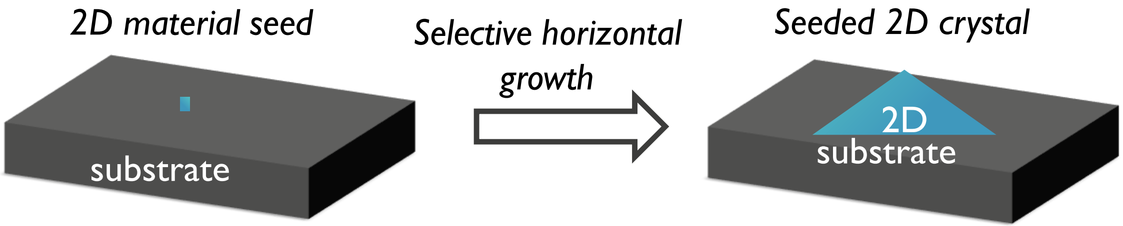
CONCLUSIONS, OUTLOOK

Versatile chemistry and anisotropic bonding of 2D materials provides unique opportunities for selective deposition, beyond the conventional concept of area selective deposition

- Area selective deposition by pattern conversion (Si → WS_2)



- Selective anisotropic growth



→ Exploit seeding of 2D crystals at well-defined locations on large area substrates embracing a better life